

PATENT SPECIFICATION

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(54) PROCESS FOR MAKING A FLEXIBLE, PLASTIC BATTERY SEPARATOR

(71) We, AMERACE CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 245 Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to flexible, microporous plastic sheets and, more particularly, to flexible, microporous plastic sheets useful as separators between the plates of electrical storage batteries.

As is well appreciated in the art, a battery separator must be porous to allow the passage of ions between the plates as well as free diffusion of acid. In addition, the battery separator must be resistant to attack by acids and electrochemical oxidation as well as being both strong and durable. More specifically, it is highly desirable that the separator be flexible enough to resist cracking during assembly since even minute cracks, if allowed to propagate during the service life of the battery, could result in premature battery failure. Moreover, the separator should be naturally hydrophilic since such battery separators do not require the addition of a wetting agent.

As disclosed for example, in the U.S. patents to Witt (2,772,322) and Selsor et al. (3,696,061), it is well known in the art to fabricate battery separators from compositions comprising a mixture of a plastic resin, an inorganic filler, and a solvent, in such a manner as to produce a microporous, semi-rigid sheet.

Attempts have been made to modify such prior art plastic based separators to increase their flexibility and thus avoid cracking during assembly and handling, by adding plasticizers to the composition being processed.

It was found, however, that the mere addition of plasticizers to these compositions resulted in separators possessing significantly inferior physical properties and particularly inferior electrochemical properties when com-

pared with non-plasticized separators. Specifically, it was observed that when plasticizers were added to such compositions the electrical resistance of the battery separator increased although the acid resistance of the resulting separator decreased.

Against the foregoing background, it is a primary objective of the present invention to provide a composition processable into a flexible, plastic-based, microporous battery separator.

It is another object of the present invention to provide a composition processable into a flexible, plastic-based, microporous battery separator resistant to cracking.

It is an additional object of the present invention to provide a composition processable into a flexible, plastic-based, microporous battery separator with good electrical resistance properties and which is resistant to attack by acid and to oxidation by electrochemicals, and, moreover, one which is normally hydrophilic and wets easily without requiring the addition of a wetting agent.

It is still another object of the present invention to provide a composition processable into a flexible, plastic-based microporous battery separator in which the plasticizer is neither leached out during processing nor during use.

It is yet still another object of the present invention to provide a composition processable into a flexible, plastic-based, microporous battery separator which is less subject to premature failure than battery separators heretofore employed.

According to the present invention there is provided a process for producing a flexible microporous battery separator from a composition comprising a thermoplastic resin binder in an amount between 10% and 16% by weight of the total composition, a plasticizer in an amount between 4% and 10% by weight of the total composition, an inorganic filler material in an amount between 19% and 23% by weight of the total composition, a solvent for said thermoplastic resin binder in an amount between 26% and 32% by weight of the total composition, and a non-

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solvent in an amount between 28% and 34% by weight of the total composition, said process including the steps of mixing said thermoplastic resin binder together with said plasticizer to form a master batch, adding to said master batch said inorganic filler material, said solvent and said nonsolvent and mixing the composition until the constituents are uniformly dispersed to form an extrudable mixture, extruding and calendering said extrudable mixture to form a sheet-like article from said composition, passing said sheet-like article through an extraction bath to remove said solvent therefrom, and drying said sheet-like article to remove said extraction medium and said nonsolvent therefrom.

The composition which is herein disclosed and which may be processed into a flexible, plastic-based, microporous battery separator, is composed of the following essential ingredients:

- a) a thermoplastic resin binder;
- b) a solvent which serves to solubilize the thermoplastic resin binder;
- c) an inorganic filler, for example silica;
- d) a nonsolvent, for example water, and
- e) a plasticizer.

The thermoplastic resin binder employed should preferably be a vinyl chloride resin binder of the "EP" or "easing processing" type which is porous and highly absorbent. This thermoplastic resin binder may be a non-plasticized vinyl chloride homopolymer resin or a copolymer of vinyl chloride admixed with a small amount (less than about 15% by weight) of a mono-ethylenic monomer such as, for example, vinyl acetate, vinylidene chloride, propylene or ethylene. A particularly preferred thermoplastic resin binder is the gamma vinyl chloride homopolymer marketed by Continental Oil Company under the trademark Conoco 5385 although good results have been obtained with the gamma vinyl chloride homopolymers marketed by the B. F. Goodrich Company under the trademark Geon 103EP and by Solvay & Cie S.A. of Belgium under the mark Solvic 229. Additionally, other thermoplastic resin binders may be used which, when admixed with a solvent, are converted into a doughy, semi-plasticized mass for easy processing and which, upon removal of the solvent, become deplasticized. Obviously, the thermoplastic resin binder selected should be chemically and physically stable under the conditions of the process of the invention and the conditions to which the final battery separator will be subjected.

The thermoplastic resin binder should comprise between 10% and 16% by weight of the total composition with a range between 11% and 15% being preferred. Particularly good results are obtained when the amount of thermoplastic resin constitutes between 11% and 12% by weight of the total com-

position and, as such, this range is most preferred.

The inorganic filler material should preferably be an inorganic solid capable of holding at least 30 parts by weight of water or other volatile matter per 100 parts by weight of nonvolatile matter and should be able to release the volatile matter upon heating to a temperature below the decomposition point of the thermoplastic resin. While any filler material capable of meeting these requirements may be employed, silica hydrogel or precipitated hydrated silica are preferred. Precipitated hydrated silica is particularly preferred and may be obtained, for example, from PPG Corporation under the trademark Hi Sil 233 or from Chemische Fabrik Hoesch of Germany under the trademark KS-300.

The inorganic filler material should constitute between 19% and 23% by weight of the total composition with a range of between 20% and 23% by weight of the total composition being preferred. When the range of inorganic filler material is between 22% and 23%, an article with particularly good physical and electrochemical properties is produced and, therefore, this range is most preferred.

The solvent employed, preferably an organic solvent, should naturally have a solvating action on the thermoplastic resinous binder and will inherently be capable of being absorbed by the filler material. While organic solvents such as, for example, acetone, ether, dimethyl formamide, orthochlorobenzene, tetrahydrofuran and certain ketones may be employed, cyclohexanone is preferred since it solubilizes polyvinyl chloride and is only slightly soluble in water.

The solvent used, preferably cyclohexanone, is employed in ranges between 26% and 32% by weight of the total composition with a range of between 26% and 30% being preferred. Particularly good results are obtained when the amount of solvent constitutes between 27% and 28% by weight of the total composition.

The nonsolvent, preferably water, constitutes between 28% and 34% by weight of the total composition with a range of between 29% and 33% being preferred. A nonsolvent in an amount ranging between 31% and 33% of the total weight of the composition has been found to produce particularly good physical properties and therefore is especially preferred.

The plasticizer selected should naturally be compatible with the other constituents and, thus, when admixed with the above mentioned compositions, be capable of improving the elongation properties of the resultant article while not adversely affecting such physical properties as electrical resistance and resistance to attack by acid or resistance to oxidation by electrochemicals. In this regard, a monomeric or polymeric plasticizer which

accomplishes these goals would be acceptable. This would include both monomeric plasticizers such as, for example, dioctyl sebacate and polymeric plasticizers such as, for example, elastomeric chlorinated polyethylene. The use of a monomeric plasticizer, and particularly dioctyl phthalate and dioctyl adipate is preferred. It has been found that articles fabricated from compositions containing either of these two monomeric plasticizers possess excellent physical and electrochemical properties.

The plasticizer constitutes between 4% and 10% by weight of the total composition with a range of between 4% and 8% being preferred. Particularly good physical properties are observed in the resultant article when dioctyl phthalate is employed in amounts between 6% and 7% by weight of the total composition and, as such, when dioctyl phthalate is the plasticizer, this range is most preferred. When, however, dioctyl adipate is the plasticizer, a range of between 4.5% and 5.5% is most preferred.

In addition to the foregoing ingredients, it will be apparent to those skilled in the art that a variety of other ingredients may be employed which do not affect the essential nature of the resultant product. Indeed, many such ingredients may be provided for the purpose of improving other properties thereof or for the purpose of improving industrial acceptance. Typical ingredients include, but are not limited to modifying or stabilizing ingredients such as, for example, carbon black and lead stearate.

An important feature of the present invention is the manner in which the ingredients are combined to form the composition capable of fabricating an article such as, for example, a flexible, plastic-based microporous battery separator.

In combining the aforementioned ingredients in the amounts and ranges specified, it has been found that the procedures recited in the aforementioned U.S. Patent No. 3,696,061 to Selsor et al. are applicable, with certain modifications. In fact, both that U.S. Patent No. 3,696,061 and U.S. Patent No. 3,696,060, assigned to the same assignees, are relevant to the subject matter of this application.

Typically a master batch of the thermoplastic resin binder and the plasticizer is first prepared by dry blending at room temperature, i.e. 65°F to 75°F, the constituent parts in a low shear solids blender such as, for example, a Patterson-Kelley high intensity "liquids solids" blender for about twenty (20) minutes. Utilization of such a blender ensures non intensive mixing and such mixing will hereinafter be defined as mixing under conditions of low shear. This is contrasted with the processes heretofore employed wherein a high shear mixer such as, for example, a Henschel mixer is used. Additionally, in

the processes heretofore employed, the thermoplastic resin binder is admixed with the plasticizer in the presence of heat to effect better absorption of the plasticizer into the thermoplastic resin binder. The Patterson-Kelley high intensity, "liquids solids" blender has a V-shaped cross-section which is preferred, although it is recognized that other mixing devices may be employed for this purpose. An aliquot of this master batch which is in damp powder form can then be placed in a clean blender and the inorganic filler, in the prescribed amount, added. The entire blend, which then resembles a dry powder, can then be admixed until all ingredients are uniformly dispersed.

It is preferred that the prescribed amount of organic solvent be then added. The rate at which the solvent is added is, however, of some importance since the maximum absorption rate of the solvent by the inorganic filler should not be exceeded lest some of the thermoplastic resin be insolubilized.

The prescribed amount of nonsolvent (e.g. water) is then added at a rate less than the maximum absorption rate of the solvent laden silica. The resultant composition is then in the form of a stable, damp, free-flowing powder.

In order to process this composition into a useful article such as, for example, a flexible, plastic-based, microporous battery separator, the composition is introduced into an extruder, preferably of a vertical screw construction, wherein the free-flowing powder is converted into a doughy mix, shaped by a sheeting die and calendered into a continuous sheet.

Extrusion temperatures may range from 80°F to 160°F with a narrower range of between 115°F and 130°F being preferred. The temperature of the die may range between 80°F and 160°F. The back-pressure of the extruder may range from between 200 psig and 500 psig with a pressure range of between 200 psig and 300 psig being preferred. Other extruders can, of course, be substituted.

The doughy mass formed within the extruder can then pass through a screen pack of about 40 mesh [Tyler Standard] and a sheeting pipe die before entering a geared down calender which is usually maintained at a temperature between 40°F and 60°F, and preferably between 40°F and 45°F. The die is locked into the calender to avoid evaporation. A calender which can be employed is a 32" calender preferably containing separator patterned rolls.

The composition, now in sheet form can then be supported on a transport screen and passed through an extraction bath, preferably a water extraction bath, the temperature of the water being normally maintained at between 120°F and 200°F although a narrower

range of between 160°F and 180°F is preferred. The sheet remains in the bath until the solvent is removed and is then dried to remove the non-solvent by conventional means. The drying temperature should normally not exceed 275°F and a temperature of 225°F is preferred.

It will be appreciated that the resultant article, after the solvent and the non-solvent constituents have been removed during processing, comprises a suitably plasticized thermoplastic resin binder forming a matrix, within and throughout which are dispersed particles of inorganic filler material. A plurality of micropores are present in the article, being formed between neighboring or adjacent particles of dispersed filler material, between individual particles of filler material and the matrix as well as within the matrix itself. These micropores are non-uniform in size, typically ranging between 0.01 microns and 100 microns, and have a mean pore diameter typically of about 1 micron as determined porosimetrically by the well-known Mercury Intrusion Method. The porosity of the resultant article when measured in alcohol, ranges between 50% and 75%.

The resultant article possesses physical properties making it ideally suited for use as a battery separator. In particular, the resultant article is not only highly porous, having a total porosity of at least 50% when measured in alcohol, but is both strong and flexible, as evidenced by its tensile strength which is generally greater than 200 psi and its elongation which is generally greater than 40%. Moreover, its electrical resistance, a characteristic of significant importance with respect to battery separators, is generally no greater than 0.070 ohms/in² and normally less than 0.040 ohms/in². When the thickness of the resultant article is reduced to, for example, about 0.025 inches, electrical resistance has been further decreased to about 0.020 ohms/in².

The following examples serve to illustrate certain preferred embodiments of the present composition and process.

Example I

In order to illustrate the preparation of a composition processable into a useable article such as, for example, a flexible, plastic-based microporous battery separator in accordance with the principles of this invention, a composition was prepared which included a plasticizer as one of its constituent parts in a ratio of 60 parts by weight of plasticizer to 100 parts by weight of thermoplastic resin binder. This composition comprised the following ingredients with its respective amounts being specified as a percentage weight of the total weight of the composition.

Ingredients	Percentage by Weight	
Conoco 5385 [Trade Mark] vinyl chloride homopolymer	11.17%	65
Diocetyl phthalate	6.67%	
Hi Sil 233 precipitated hydrated silica filler	22.20%	
Cyclohexanone	27.76%	
Water	32.20%	70
Carbon black	.001%	

The composition was prepared by first dry blending in a Patterson-Kelley high intensity "liquids solids" blender the Conoco 5385 with the diocetyl phthalate to form a master batch and then adding the Hi Sil 233 followed by the cyclohexanone, water and carbon black.

The resultant composition was then introduced into a vertical Aragon extruder with a stainless steel screw having a compression ratio of about 1.4/1. The composition was extruded at a temperature of about 120°F and at a pressure of about 250 psig. A 32" calender with a calender top, pattern separator roll was employed to produce a separator patterned sheet approximately 0.100 inches thick. The resultant sheet was then passed through a water extraction tank in which the water temperature was maintained at about 160°F and then dried in an air dryer at an air temperature of about 225°F.

The resultant fabricated article, in this instance, a flexible, microporous, battery separator, had the following physical properties:

Tensile Strength	210 psi	
Elongation	65%	
Mullen Strength	64 psi	
Electrical Resistance	0.054 Ω /in ²	
Total Porosity (Mercury Intrusion Technique)	1.04 cc/g	100
Mean Pore Diameter	0.085 μ	
% of Pores >20 μ	2.5%	

Of the tests performed, the tensile strength, elongation, and Mullen strength data indicated that the resultant article was sufficiently strong and flexible to withstand any damage inflicted during assembly and eventual use.

The electrical resistance and porosity data indicated a product with a fine pore size which possessed excellent electrochemical properties. For use as a battery separator, electrical resistance should be as low as possible, preferably less than about .070 Ω in². The resultant product's electrical resistance of .054 Ω in² was, therefore, more than adequate. Additionally, the data with respect to pore size and total porosity indicated that while the pore size and distribution was in the microporous range, the resultant article was highly

porous. A mean pore diameter of one micron or less is preferred. Further, this data indicated that virtually no plasticizer leached out during processing. The resultant product was hydrophilic and displayed good acid resistance.

Example II

In order to demonstrate the effects of practicing the instant invention with a lower ratio of plasticizer to thermoplastic resin, the same procedure as set forth in Example I was repeated with the following ingredients in the following percentages wherein the ratio of plasticizer to thermoplastic resin was 50 parts by weight of plasticizer to 100 parts by weight resin:

Ingredients	Percentage by Weight
Conoco 5385 vinyl chloride homopolymer	10.98%
Diocetyl phthalate	5.49%
Hi Sil 233 precipitated hydrated silica filler	21.97%
Cyclohexanone	28.61%
Water	32.95%
Carbon black	.001%

The resultant composition was fabricated into a useful article such as, for example, a flexible, microporous battery separator, in the same manner as in Example I and the resultant article had the following physical properties:

Tensile Strength	219 psi
Elongation	54%
Mullen Strength	53 psi
Electrical Resistance	0.041 Ω/in^2
Total Porosity (Mercury intrusion Test)	0.99 cc/g
Mean Pore Diameter	0.095 μ
% of Pores > 20 μ	2.5%

The results of these physical tests indicated a product with properties essentially similar to the composition in Example I although the elongation figures reflected the fact that the resultant article was somewhat less flexible than the article in Example I and had a slightly higher electrical resistance. The resultant article, however, was a commercially acceptable, flexible, plastic-based microporous battery separator.

Example III

In order to illustrate the preparation of a composition according to the present invention wherein different types of thermoplastic resin and inorganic filler materials were employed although with the same ratio of resin to plasticizer as in Example II, the same procedure as set forth in Example I was repeated with the following ingredients in the following percentages:

Ingredients	Percentage by Weight	
Solvic 229 vinyl chloride homopolymer	14.23%	65
Diocetyl phthalate	7.11%	
KS 300 precipitated hydrated silica filler	19.96%	
Cyclohexanone	28.22%	70
Water	30.48%	
Carbon black	0.001%	

The resultant composition was fabricated into a useful article such as, for example, a flexible microporous battery separator in the same manner as in Example I and the resultant article had the following physical properties:

Tensile Strength	290 psi	80
Elongation	57%	
Mullen Strength	68 psi	
Electrical Resistance	0.045 Ω/in^2	85
Total Porosity (Mercury Intrusion Test)	0.87 cc/g	
Mean Pore Diameter	0.11 μ	
% of Pores > 20 μ	3.5%	

In comparing the physical data of this article to the article produced in Example I, the tensile strength of the article was higher than the article of Example I, although its elongation was less, indicating a stronger, but less flexible product. The electrical resistance of the article was lower than the electrical resistance of the article of Example I. Further, the porosity of the article was less than the porosity of the article of Example I although the pore size was generally greater.

Example IV

In order to illustrate the preparation of a composition according to the present invention wherein the type of plasticizer was changed, the same procedure as set forth in Example I was repeated wherein diocetyl adipate was chosen as the plasticizer and used in a ratio of 50 parts by weight of plasticizer to 100 parts by weight of resin. Additionally, a different thermoplastic resin was employed. The following ingredients in the following percentages were employed:

Ingredients	Percentage by Weight	
Geon 103EPF 10 thermoplastic resin	11.01%	110
Diocetyl adipate	4.96%	
Hi Sil 233 precipitated hydrated silica filler	22.03%	
Cyclohexanone	29.52%	115
Water	32.48%	
Carbon black	0.001%	

The resultant composition was fabricated into a useful article such as, for example, a

flexible, microporous battery separator, in the same manner as in Example I and the resultant article had the following physical properties:

5	Tensile Strength	187 psi
	Elongation	62%
	Mullen Strength	60 psi
	Electrical Resistance	.031 Ω /in ²
10	Total Porosity (Mercury Intrusion Test)	0.07 cc/g
	% of Pores >20 μ	1.3%

The physical data illustrate that the use of dioctyl adipate as a plasticizer produced an article with both physical and electrochemical properties quite similar to the article of Example I wherein dioctyl phthalate was the plasticizer employed.

WHAT WE CLAIM IS:—

1. A process for producing a flexible microporous battery separator from a composition comprising a thermoplastic resin binder in an amount between 10% and 16% by weight of the total composition, a plasticizer in an amount between 4% and 10% by weight of the total composition, an inorganic filler material, in an amount between 19% and 23% by weight of the total composition, a solvent for said thermoplastic resin binder in an amount between 26% and 32% by weight of the total composition, and a nonsolvent in an amount between 28% and 34% by weight of the total composition, said process including the steps of mixing said thermoplastic resin binder together with said plasticizer to form a master batch, adding to said master batch said inorganic filler material, said solvent, and said nonsolvent and mixing the composition until the constituents are uniformly dispersed to form an extrudable mixture, extruding and calendering said extrudable mixture to form a sheet-like article from said composition, passing said sheet-like article through an extraction bath to remove said solvent therefrom, and drying said sheet-like article to remove said extraction medium and said nonsolvent therefrom.

2. A process as claimed in claim 1, wherein the ingredients in the master batch are mixed together under conditions of low shear and without the addition of heat.

3. A process as claimed in claim 2, wherein the ingredients of said extrudable mixture are mixed together under conditions of low shear without the addition of heat.

4. A process as claimed in claim 3 wherein the extrudate is calendered to form said sheet-like article.

5. A process as claimed in claim 4, wherein said low shear mixing steps are carried out at a temperature between 65°F and 75°F, wherein said extruding step is carried out at a temperature of between 80°F and 160°F at a backpressure within the range of 200 psig and 300 psig, and wherein said extraction medium comprises a water bath at a temperature in the range of 120°F to 200°F.

6. A process as claimed in claim 1, wherein said plasticizer is dioctyl phthalate or dioctyl adipate.

7. A process as claimed in claim 6, wherein said thermoplastic resin binder is a polyvinyl chloride resin, said inorganic filler is silica, said solvent is cyclohexanone, and said nonsolvent is water.

8. A process as claimed in claim 7, wherein said polyvinyl chloride resin is a vinyl chloride homopolymer, present in an amount between 11% and 12% by weight of the total composition, wherein said plasticizer is dioctyl phthalate present in an amount between 6% and 7% by weight of the total composition, wherein said silica filler material is present in an amount between 22% and 23% by weight of the total composition, wherein said cyclohexanone is present in an amount between 27% and 28% by weight of the total composition, and wherein said water is present in an amount between 31% and 33% by weight of the total composition.

9. A process as claimed in claim 7, wherein said polyvinyl chloride resin is a vinyl chloride homopolymer present in an amount between 11% and 12% by weight of the total composition, wherein said plasticizer is dioctyl adipate present in an amount between 4.5% and 5.5% by weight of the total composition, wherein said silica filler is present in an amount between 22% and 23% by weight of the total composition, wherein said cyclohexanone is present in an amount between 26% and 30% by weight of the total composition, and wherein said water is present in an amount between 31% and 33% by weight of the total composition.

10. A process according to claim 1 for producing a flexible microporous battery separator substantially as hereinbefore described.

11. A flexible, microporous, battery separator when produced by a process according to any one of claims 1 to 10.

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